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BIOPCM THERMOPHYSICAL CHRACTERIZATION THROUGH THE T-HISTORY METHOD

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Abstract. *The Latent thermal energy storage role in building demand control is gaining popularity as intermittent energy sources, such as solar photovoltaic or wind turbines, become more popular. In order to succeed, new suitable phase change materials (PCM) need to be identified and characterized. This paper presents the thermophysical characterization of a seven BioPCMs (6 waxes and one oil) through the T-history methodology. The method consists of comparing the temperature curve of the BioPCM sample in relation to the water temperature curve and thus determining some calorimetric properties of the materials analyzed. The experimental apparatus was locally developed for this purpose and proved to be suitable for the thermal characterization of BioPCMs with melting points below 100°C..*
Keywords: *Latente Thermal Storage , T-history, BioPCM, Calorimetry.*

1. INTRODUCTION

The latent thermal energy storage role in building demand control is gaining popularity as intermittent energy sources, such as solar photovoltaic or wind turbines, become more popular (Zang et al., 2015 and Osório et al., 2015). In order to succeed, new suitable phase change materials (PCM) need to be identified (Kalnaes and Jelles., 2015 and Cunha and Eames, 2016). As an alternative to more traditional options, BioPCMs are gaining popularity due its wide variety of phase change temperatures, thermal and chemical stability and the fact that they can are obtained from natural, less pollutant, sources. This study chose six organic waxes and one oil to be characterized in order to evaluate their feasibility as PCM. Unlike paraffins, which are byproducts of petroleum, the coconut oil and the vegetable waxes can be produced from local renewable resources, taking advantage of Brazilian's favorable climate, its territorial extension and the diversity of its flora, making them great candidates for PCM applications with low carbon footprint.

Although traditional methods for determining the heat of fusion, specific heat and melting point of PCMs are well established, the samples tested tend to be in the range between 1 to 10 milligrams. As BioPCMs are commonly formed by the combination of two or more fatty acids, these methods, such as differential scanning calorimetry (DSC) may deliver results different from the observed by bulk materials. For this reason, alternative methodologies are under development, such as the T-history (Cabeza et al., 2015), first presented by Yinping et al. (1999).The method consists into comparing the temperature curves of a PCM material, which goes through a phase change process, against the one from a known reference (usually water) and processing this data into calorimetric information such as phase change enthalpy, specific heat and thermal conductivity.

This study presents the findings from applying the T-history method to BioPCMs within two different phase change temperature ranges. One of them, the coconut oil, may be suitable for space cooling applications while the second, a range of organic wax, may be applied to space or water heating applications.

2. METHOD DESCRIPTION

The T-history method was developed and proposed by Yinping, et al. (1999) for the thermophysical characterization of PCMs. In that paper, the authors reviewed the methods of conventional calorimetry and presented their limitations for phase change material analysis, like the sample volume being too different from the one utilized into bulk applications, ignoring some of the heterogeneity presented in this kind of material, as well as the high costs of the equipment.

Due to these factors, the authors developed a simpler T-history method for the determination of melting point, subcooling degree, specific heat and thermal conductivity of different PCM samples simultaneously. The method is especially indicated for the characterization of PCMs for thermal energy storage applications (Yinping et al., 1999).

Later studies presented some modifications over the original experimental configuration or mathematical model such as the ones presented by Hong et al. (2004), Lazaro et al. (2006), Mazo et al. (2015), Solé et al. (2013) among others.

2.1 Determination of the heat of fusion, specific heat and so on of PCMs

In the method developed by Yinping et al. (1999), a reference sample and the PCMs being characterized are heated above their phase change temperature and suddenly exposed to room temperature. A data logger records the temperature variation during the process, creating its history as shows in Fig.1 and Fig. 2.

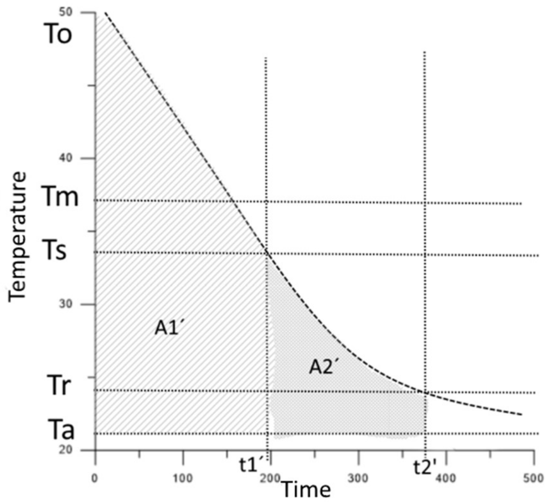

Figure 1 – Temperature curve water

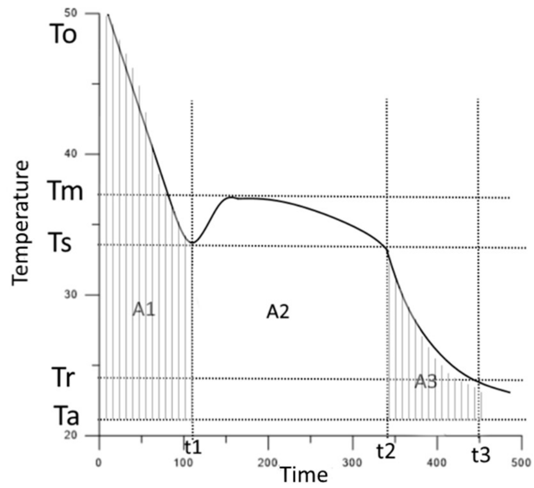

Figure 2 – Temperature curve PCM

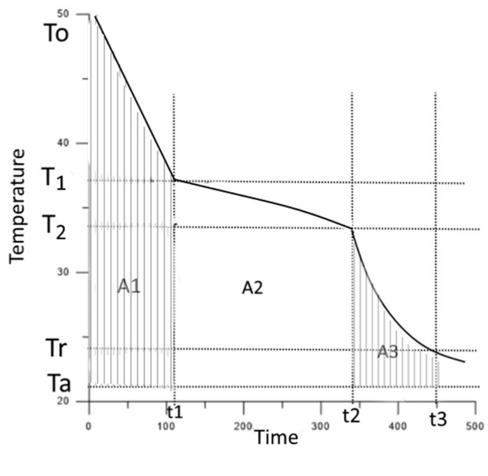

Figure 3 – Temperature curve PCM without subcooling

Yinping assumes that when the Biot number ($Bi = hR / 2k$, where R is the radius of a tube , k the thermal conductivity of PCM and h the natural convective heat transfer coefficient of air outside tube) is less than 0.1, the temperature distribution in the sample can be considered uniform and the lumped capacitance method can be used. Thus, the author assumes that:

$$\left(m_t c_{p,t} + m_p c_{p,l}\right)(T_0 - T_s) = hA_c A_1 \ , \qquad (1)$$

where, m_p and m_t are respectively the masses of the PCM and the tube, $c_{p,l}$ and $c_{p,t}$ are the mean specific heat of the liquid PCM and of the material of the tube, A_c is the convective heat transfer area of a tube and $A_1 = \int_0^{t_1} (T - T_{\infty,a})\, dt$. Additionally,

$$m_p H_M = hA_C A_2 \tag{2}$$

where H_m is the heat of fusion of the PCM, $A_2 = \int_{t_1}^{t_2} (T - T_{\infty,a})\, dt$ where t_1 and t_2 is are the moments where the phase change process starts and ends, respectively . After, we have:

$$\left(m_t c_{p,t} + m_p c_{p,s}\right)(T_s - T_r) = hA_c A_3, \tag{3}$$

where $C_{p,s}$ is the mean specific heat of solid PCM , $A_3 = \int_{t_2}^{t_3} (T - T_{\infty,a})\, dt$ and T_r is the reference temperature.

Similarly, for the water sample we have:

$$\left(m_t c_{p,t} + m_w c_{p,w}\right)(T_0 - T_s) = hA_c A_1' \text{ , and} \tag{4}$$

$$\left(m_t c_{p,t} + m_w c_{p,w}\right)(T_s - T_r) = hA_c A_2' \text{ ,} \tag{5}$$

where m_w and $c_{p,w}$ are the masses and the mean specific heat of water, $A_1' = \int_{t_0}^{t_1'} (T - T_{\infty,a})\, dt$ and $A_2' = \int_{t_1}^{t_2'} (T - T_{\infty,a})\, dt$.

Through the equations presented, we have

$$c_{p,s} = \frac{m_w c_{p,w} + m_t c_{p,t}}{m_p} \frac{A_3}{A_2'} - \frac{m_t}{m_p} c_{p,t} \quad , \tag{6}$$

$$c_{p,l} = \frac{m_w c_{p,w} + m_t c_{p,t}}{m_p} \frac{A_1}{A_1'} - \frac{m_t}{m_p} c_{p,t} \quad \text{, and} \tag{7}$$

$$H_m = \frac{m_w c_{p,w} + m_t c_{p,t}}{m_p} \frac{A_2}{A_1'} (T_0 - T_s) \quad . \tag{8}$$

For PCMs without supercooling (Fig.3), the equations to $c_{p,s}$ and $c_{p,l}$ are the same, however the heat of fusion is rewritten as

$$H_m = \frac{m_w c_{p,w} + m_t c_{p,t}}{m_p} \frac{A_2}{A_1'} \left(T_0 - T_{m,1}\right) - \frac{m_t c_{p,t}(T_{m,1} - T_{m,2})}{m_p}. \tag{9}$$

2.2 Determination of the thermal conductivity of PCMs

For the determination of the thermal conductivity a tube containing the melted PCM at temperature T_0, slightly higher than T_m, must be suddenly dipped into a cool water bath at temperature lower than T_m. According to the authors, if the ratio of the length to the diameter of the tube is larger than 15, we can assume that the heat transfer is one dimensional. Thus, the heat diffusion equation for the cylinder is

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\,\frac{\partial T(r,t)}{\partial r}\right) = \frac{1}{\alpha_p}\frac{\partial T(r,t)}{\partial t} \qquad (\xi < r < R,\ t > 0)\ , \tag{10}$$

with a boundary condition

$$k_s \left.\frac{\partial T}{\partial r}\right|_{r=R} = h_w (T_\infty - T) \qquad t > 0 \tag{11}$$

and the initial condition

$$T(\xi = R) \cong T_m \qquad t = 0, \tag{12}$$

where T(r,t) is the temperature of the PCM sample at radius r and instante t, α_p is the termal diffusivity of the PCM, ξ is the radius of the interface between the liquid and solid phases and h_w is the coefficient for convective heat transfer from the tube to the stirred cool water.

For the interface, we have

$$T(r = \xi) = T_m \tag{13}$$

$$k_s \left.\frac{\partial T}{\partial r}\right|_{r=\xi} = \rho_p H_m \frac{\partial \xi}{\partial t} \quad . \tag{14}$$

Using the perturbation method and neglecting the second order term of the expansion, we have the effective thermal conductivity of the solid PCM

$$k_s = \left[1 + \frac{c_p(T_m - T_{\infty,w})}{H_m}\right] \Big/ \left[4\left(\frac{t_f(T_m - T_{\infty,w})}{\rho_p R^2 H_m} - \frac{1}{h_w R}\right)\right], \tag{15}$$

where ρ_p is the density of the PCM and t_f is the time of full solidification of the PCM.

The equation for determination of the k_l (the thermal conductivity of the liquid PCM) can be obtained for a PCM in the solid state placed into a hot water bath.

3. EXPERIMENTAL PROCEDURE

For the determination of the thermophysical properties of the PCMs studied in this paper, an experimental setup was developed (Fig. 6). In order to produce the required information, a bespoke electronic circuit was created, utilizing an Arduino board and a group of thermocouples (type-K)(Fig.5). The sensors were inserted into the test tubes, containing the PCM and the reference material (distilled water). One additional thermocouple was utilized to measure the ambient temperature. The data logger was set to read and store the measured temperature at every 10 seconds in order to produce the temperature profile.

All the tubes were filled with the same volume of material, with 9/10th of their capacity in order to allow the insertion of the covers. Before starting the experiment, it was required to gather physical data from each sample, such as density and total mass. For the last, a radwag analytical scale (precision 0,1mg) was utilized while the density was found by measuring the mass of the sample material inside a 50mL picometer (±0,001mL).

Finally, initial results proved that in order to produce consistent data, the type-K thermocouples should be positioned in the centre of the tubes diameter. Touching or being too close to the glass walls produced incoherent data.

Both the PCM and the reference samples were brought to the initial condition by inserting the test tubes into a hot water bath above the melting point.

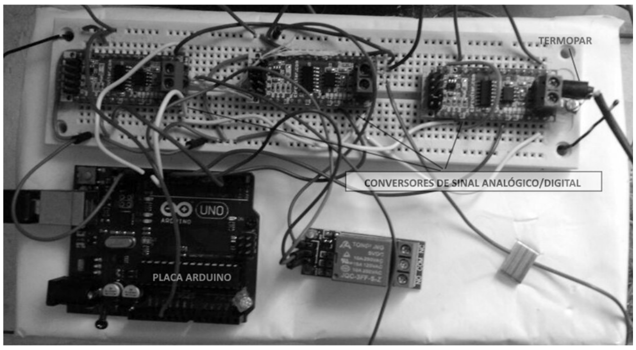

Figure 4 – Arduino circuit

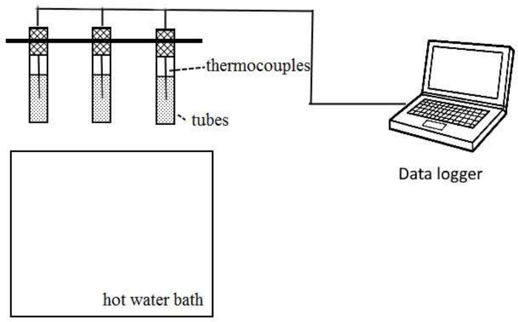

Figure 5 – System setup

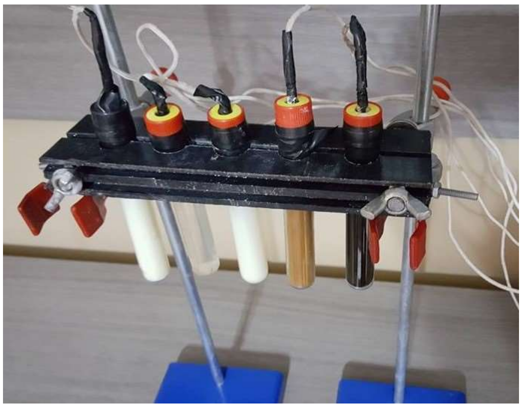

Figure 6. Test tube support

The uncertainties of the measured results are dependent of the uncertainties associated to each measurement method. Moffat (1988) show that uncertainties in a result can be estimated using a root sum square combination of the uncertainty of each of the individual inputs. For example, given R(X1,X2,…,Xn), the uncertainty may be estimated as:

$$\delta R = \sqrt{\sum_{i=1}^{n} \left(\frac{\partial R}{\partial X_i} * \delta X_i \right)^2} \qquad (16)$$

Applying this method to the specific heat calculation it was observed that the results are considerably sensitive to factors related to the area formed below the temperature curve, as highlighted in the picture below.

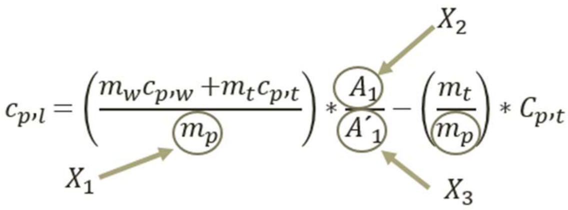

Figure 7. main uncertainty sources

For the current setup, it was observed an uncertainty of around 10,1%. Improvements are under way, including lower time steps between temperature measurements and a new circuit, which should reduce uncertainty to at least 7% but were not ready for the current experiments.

4. RESULTS AND DISCUSSION

The T-history methodology was applied to four different materials: coconut oil, palm wax, carnauba wax 3 and carnauba wax 4. The coconut oil was chosen as the first material to be tested as reference values for its properties are available in the literature, working as a guideline regarding the results reliability.

4.1 Coconut oil analysis

In addition to the adjustments described in the experimental procedure section, the first tests proved that the cooling rate had influence over the results, phenomenon also reported in the DSC literature, such as in the research conducted by Tan et al. when studying coconut oils (TAN; MAN, 2016) Consistent results were only observed with rates below 5°C per minute (assuming only the period before the subcooling). For this reason, an air chamber was utilized instead of a water bath to cool the samples. The Figure 8 represents the temperature curve produced during the cooling process.

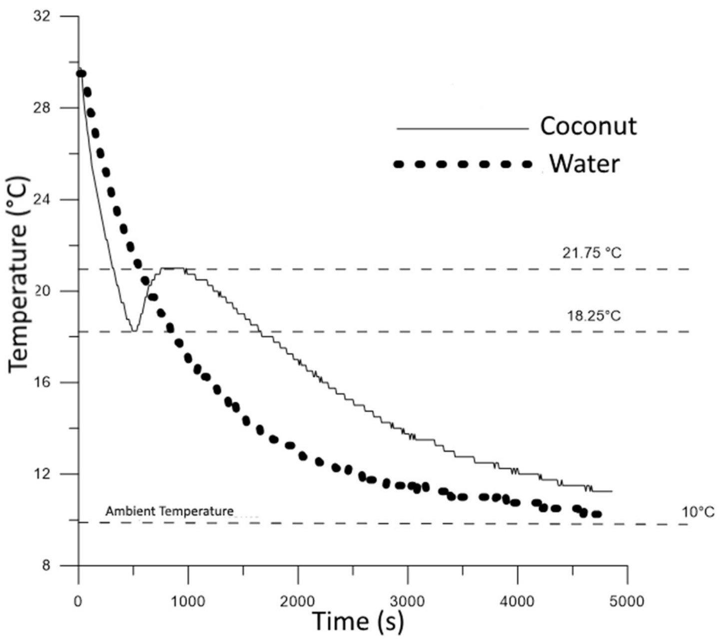

Figure 8. Coconut oil T-history curve

After applying the gathered information into the data analysis methodology developed by Yinping et al, the Table 1 was built.

Table 1. Experimental results for flexural properties of CFRC-4HS and CFRC-TWILL composites.

	Found value	Reference Value
Phase Change Temperature	21,75 °C (± 0,33 °C)	Entre 21°C (TIPVARAKARNKOON , 2008) and 24°C (TAN; MAN, 2002)
Specific Heat	2,3 kJ/kgK (± 0,1 kJ/kgK)	2,1 kJ/kgK (METTAWEE, EAD, 2013)
Heat of fusion	104,32 kJ/kg (± 17 kJ/kgK)	103 kJ/kg (TAN; MAN, 2002), 198 kJ/kg (LEE, 2016)

The T-history method was also used to estimate the conductivity of the material. The found value, 0,188 W/(mK), is in agreement with expected range (BioPCMs usually have conductivity between 0,1 and 0,2 W/(mK) (SOLÉ et al., 2013) and the coconut oil conductivity found into the literature, 0,166 W/(mK) (LEE et al, 2016).

It can be observed that the heat of fusion found is just below the value found in commercially available paraffinic PCMs (DIECKMAN, 2016), indicating that although it may be used as latent heat storage medium, it may require more volume than more traditional PCMs. Nevertheless, it can be produced from renewable sources, meaning that even more volume is required, the resulting carbon footprint can be significantly low.

4.2 Vegetables waxes analysis

The same methodology previously presented was applied to the waxes, which have melting temperature well above the ambient temperature. The T-history curves produced at different runs for the Palm wax, the Carnauba wax 3 and the Carnauba Wax 4 can be visualized in Fig. 9, Fig. 10 and Fig. 11 respectively.

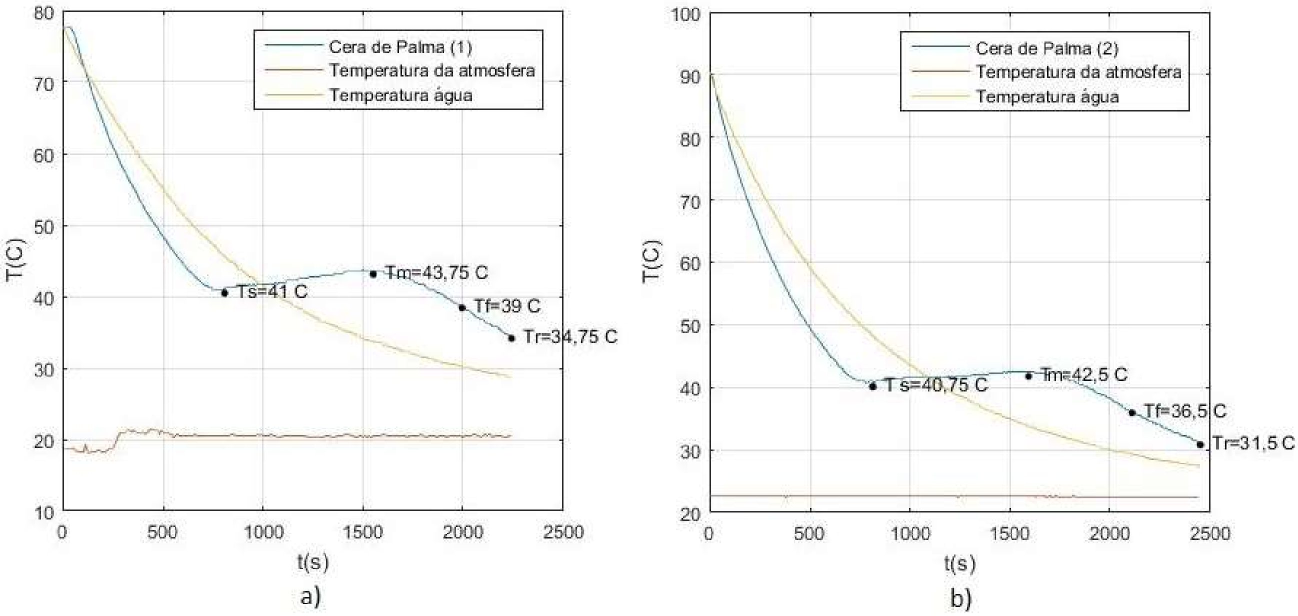

Figure 9. Palm Wax

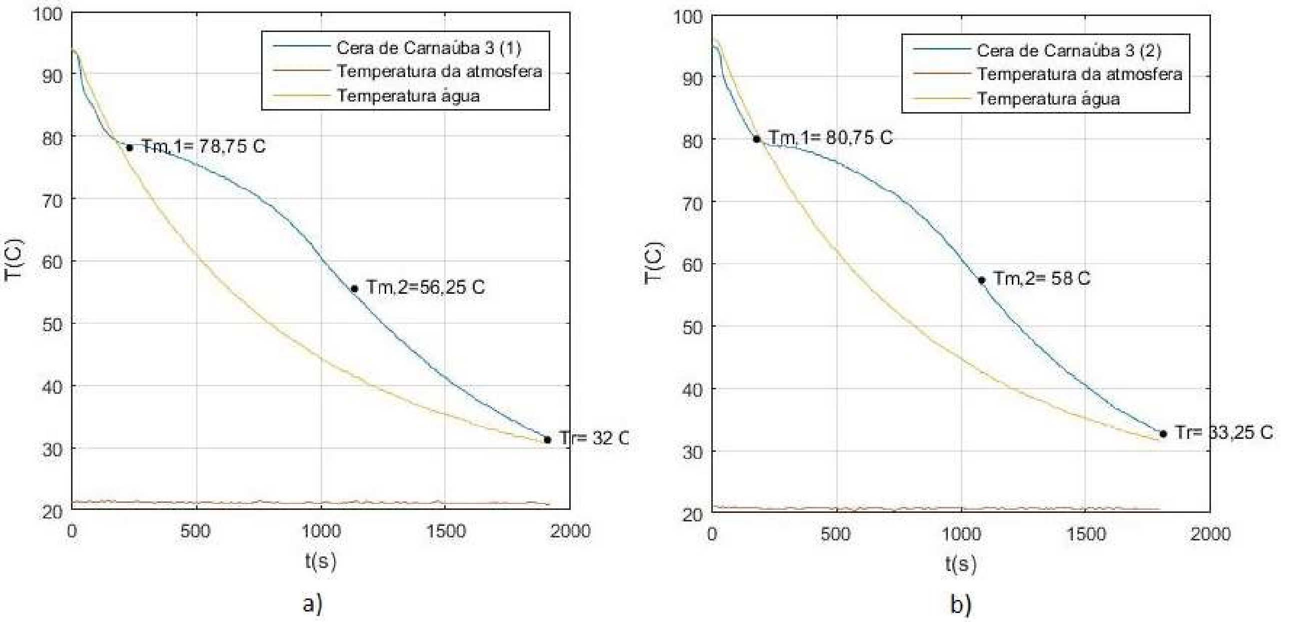

Figure 10. Carnauba 3 Wax

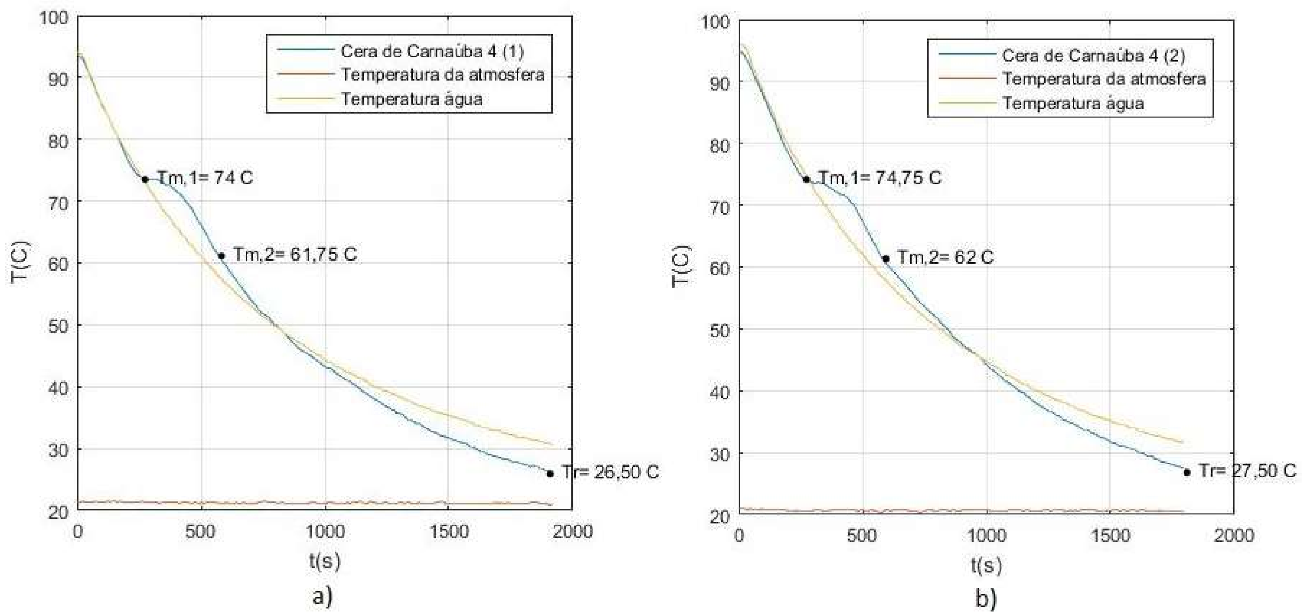

Figure 11. Carnauba 4 Wax

The difference in the curves produced for the same material is explained by the difference in the ambient temperature to which the waxes were exposed in order to cool. It did not affect the overall results regarding the found properties, as show in Tab 2.

It was verified that Carnauba wax 3 has a higher enthalpy of fusion among the studied PCMs. It is interesting to notice that it has higher storage capacity per volume of phase changing material than many of currently commercially available PCMs (DIECKMAN, 2016). It means that its use can reduce the required storage volume, when compared with most paraffin, and carbon footprint, as the material can be produced from renewable sources.

Table 2. Experimental results for wax T-history characterization

Material	T_m (ºC)	$c_{p,l}$ (kJ/kg K)	$c_{p,s}$ (kJ/kg K)	H_m (kJ/kg)
Palma (1)	43,75	3,197	1,011	127,7
Palma (2)	42,5	2,820	1,613	141,383
Carnaúba 3 (1)	78,75 – 56,25	5,277	1,509	273,127
Carnaúba 3 (2)	80,75- 58	3,953	1,421	267,519
Carnaúba 4 (1)	74 - 61,75	4,653	2,687	91,709
Carnaúba 4 (2)	74,75 – 62	4,273	2,848	89,663

5. CONCLUSIONS

The experimental apparatus and methodology developed proved suitable for thermal characterization of low temperature phase change BioPCM as it was utilized to characterize a coconut oil and three vegetable waxes. The found melting enthalpy for all studied materials are within the expected range and, as current studies indicate, suitable for building demand control (KOSNY;SHUKLA;FALLAHI, 2013).

Future works aims to reduce system uncertainty, focusing into improving the thermopair precision and t-history curve analysis by rebuilding the data logger, including new calibration, and reducing the time step between each measurement, which, combined, may reduce uncertainty in at least 3%.

Said that, the reference methodology and built apparatus proved to be appropriate for thermophysical characterization of BioPCMs, allowing the development of applied studies with this kind of material at reduced equipment costs.

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7. RESPONSIBILITY NOTICE